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Electrochemical Techniques for Characterization and Detection Application of Nanostructured Carbon Composite

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1. Introduction

Nowadays, the introduction of nanomaterials within sensors composition has been shown a growing interest because they offer exciting new opportunities in the field of sensing based on their fascinating properties.

Nanostructured carbon in forms of carbon nanotubes and carbon nanofibers represents the most commonly studied nanostructured materials in sensor obtaining. Single-wall carbon nanotubes and multi-wall carbon nanotubes forms of carbon nanotubes have been studied more extensively in comparison with carbon nanofibers for the sensing applications based on their more sensitive properties. However, both forms of nanostructured carbon exhibit great potential for use as unmodified or modified electrode for the detection applications [1,2].

It is well-known that the carbon based sensors/electrodes are widely used in electroanalytical applications because of the properties of the carbon materials, *i.e.*, large potential window, low background current, low cost, versatile surface chemistry, suitability for various sensing applications [1-5]. Carbon-nanotubes and carbon nanofibers based electrodes are very promising for the detection of inorganic and organic compounds [1, 2, 6-18]. However, for certain electroanalytical requirements in relation with the detection of various target analytes as individual, selective or simultaneous detection the nanostructured carbon electrode should be modified with suitable nanoparticles, *e.g.*, silver and copper nanoparticles. Almost all of the electrochemical sensors made up of unmodified/modified nanostructured carbon materials could be applied for the detection of analytes ranging from chemical to biological molecules [6-26].

Several detection applications using carbon nanotubes and nanofibers and silver/copper nanoparticles-modified carbon nanotubes electrodes are summarized in Table 1.

Electrode type	Target analyte	Reference
Carbon nanotubes	H ₂ O ₂	[6]
	Bi (III)	[7]
	As(III), Pb (II)	[43]
	Valocyclovir	[10]
	Carbohydrates	[12], [13]
	Phenol derivates	[14], [15], [16]
	Butylparaben	[18]
Carbon nanofibers	H ₂ O ₂	[2]
	Phenol derivates	[17]
Silver-modiefied carbon nanotubes	Ibuprofen	[23]
	Dopamine, ascorbic acid	[26]
Copper-modified carbon nanotubes	Glucose	[22], [24]
	Ammonia	[25]

Table 1. Various inorganic and organic species detected at carbon nanotubes and nanofibers and silver/copper nanoparticles-modified carbon nanotubes electrode materials.

This chapter is focused to present the unmodified/modified nanostructured carbon composite electrode correlated with different types of electrochemical techniques, i.e., cyclic voltammetry (CV), differential-pulsed voltammetry (DPV), square-wave voltammetry (SWV), chronoamperometry (CA) and pulsed amperometry (PA), applied for sensing application as voltammetric/amperometric sensors. The electrochemical detection performance is directly linked to the electrochemical properties of electrode surface in conjunction with the specific electrochemical techniques. The electroanalytical performance for voltammetric/amperometric detection applications of the nanostructured carbon composite (NCC) and metallic nanoparticle-modified nanostructured carbon composite (M-NCC) electrodes, i.e., carbon nanotubes-epoxy (CNT), carbon nanofiber-epoxy (CNF), silver nanoparticles-electrodecorated carbon nanotubes-epoxy (AgCNT), silver nanoparticles-electrodecorated carbon nanofibers-epoxy (AgCNF), copper nanoparticles-electrodecorated carbon nanotubes-epoxy (CuCNT), copper nanoparticles-electrodecorated carbon nanofibers-epoxy (CuCNF), are discussed and presented in this chapter. CV technique is applied for the electrochemical characterization of composite electrodes based on the carbon nanotubes and nanofibers within epoxy matrix synthesised by two-roll mill method in order to use them for the detection applications. Also, M-NCC electrodes are characterised and tested comparatively to improve the electroanalytical performance in the detection applications.

2. Nanostructured carbon based composite (NCC) and metallic nanoparticles-modified nanostructured carbon composite (M-NCC) electrodes

Taking into consideration the main advantage of the composite electrode due to the specific behavior of ensemble/array of microelectrodes, which are characterized by significant higher useful currents due to the large surface area [27], the nanostructured carbon-based composite (NCC) electrodes represent the new generation with the enhanced properties. The most representative and often used of the nanostructured carbon composite materials are nanofibers and nanotubes [21, 28]. Also, metallic nanoparticles decorated on the composite electrode have been studied for various applications [22, 23].

Various detection and sensing applications of NCC electrodes have been extensively studied due to their interesting mechanical, electrical and electrochemical properties [4, 5, 9, 15, 29].

A major importance is given by the composite electrode obtaining, which is responsible for the NCC electrode properties and further detection/sensing applications.

The development of composites electrodes consisting of conductive nanostructured carbon phases dispersed within polymeric matrices has led to important advances in analytical electrochemistry and sensor devices. These new electrode materials combine the electrical properties of carbon with the ease of processing of resins and show attractive electrochemical, physical, mechanical, and economical features [19, 20, 30, 31]. The application of metallic nanoparticles has been shown a raised interest in the field of electrochemistry, in particular in electroanalysis due to their enhanced optical, electronic, magnetic and catalytic properties. Also, in terms of electroanalysis the metallic nanoparticles materials are appropriate to modify electrodes due to several advantages, *e.g.*, high active surface area, enhanced selectivity, and improved mass transport [32-34].

Based on the composite classification, the composite electrodes discussed in this chapter belong to randomized ensembles, in which nanostructured carbon is mixed with epoxy resin, after its dispersion in a suitable solvent (Figure 1). Tetrahydrofuran (THF) and N, N-dimethylformamide (DMF) are efficient solvents for a good dispersion of carbon nanofibers (CNFs) and carbon nanotubes (CNTs) to avoid their agglomeration [15, 22, 23]. Various obtaining methods have been developed to deposit metal nanoparticles on various substrates to obtain so-called chemically modified electrodes (CMEs) characterized by enhanced properties for detection/sensing applications. The most common metal nanoparticles used are copper, silver, gold, and platinum, and as well as the most frequently methods encountered in literature are in respect to the pathway of metallic nanoparticles deposition. Thus, the chemical synthesis is referred at the reduction with different reagents, UV light or electron-beam irradiation [35-37]. Also, the deposition of metallic nanoparticles can be performed by electrochemical techniques [38]. The electrochemical deposition method provides an easy and rapid alternative for the preparation of metallic nanoparticles based electrodes within a short period of time. In addition, this technique present some advances over chemical method such as high purity of

the particles, higher control over the dimension, lower particle size distribution, more control over the density [39-41].

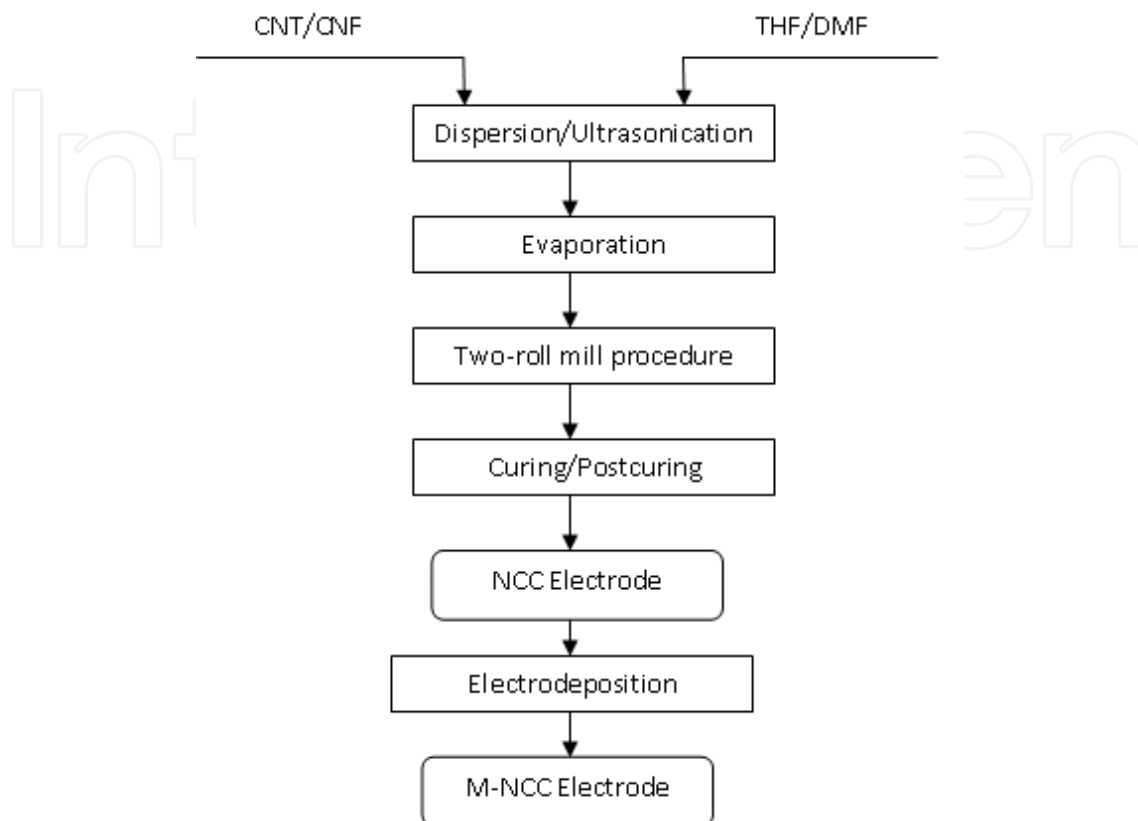


Figure 1. Schematic diagram of M-NCC-electrode preparation; metallic nanoparticles obtaining by electrodeposition.

Another main aspect is to distribute nanostructured carbon within epoxy matrix to reach the composite electrodes. Scanning electron microscopy (SEM) technique is very useful to evaluate the dispersion of the carbon filler within epoxy, which is responsible by the surface morphology and the structure and as consequence, the electrical and electrochemical properties of the NCC electrode (Figure 2). Also, the metallic nanoparticles can be observed and measured by this technique. Using two-roll mill procedure to obtain NCC electrode is very simple and assures a good dispersion and homogeneous distribution of nanostructured carbon filler within epoxy matrix (Figure 2 a, b). The electrochemical techniques used for the electrodeposition influenced also, the nanoparticles size and distribution on the conductive carbon filler. Thus, by maintaining the electrode potential at a certain value, e.g., -0.4 V/SCE for Ag in AgNO_3 supporting electrolyte, which is assured by chronoamperometry (CA) technique (described in subchapter 3.1), a spontaneous formation of silver nanoparticles on NCC surface occurred, which are deposited in aggregated form. Ag particles are distributed randomly on the electrode surface and characterized by various sizes (see Figure 2c-e). Better distribution and homogeneous sizes of Ag nanoparticles are achieved if cyclic voltammetry (CV) (described in subchapter 3.4) is applied by successive running within a certain potential range (Figure 2 f).

The electrode surface morphology, structure and nanoparticles sizes influence the electrical and electrochemical properties of the NCC electrode envisaging their detection applications.

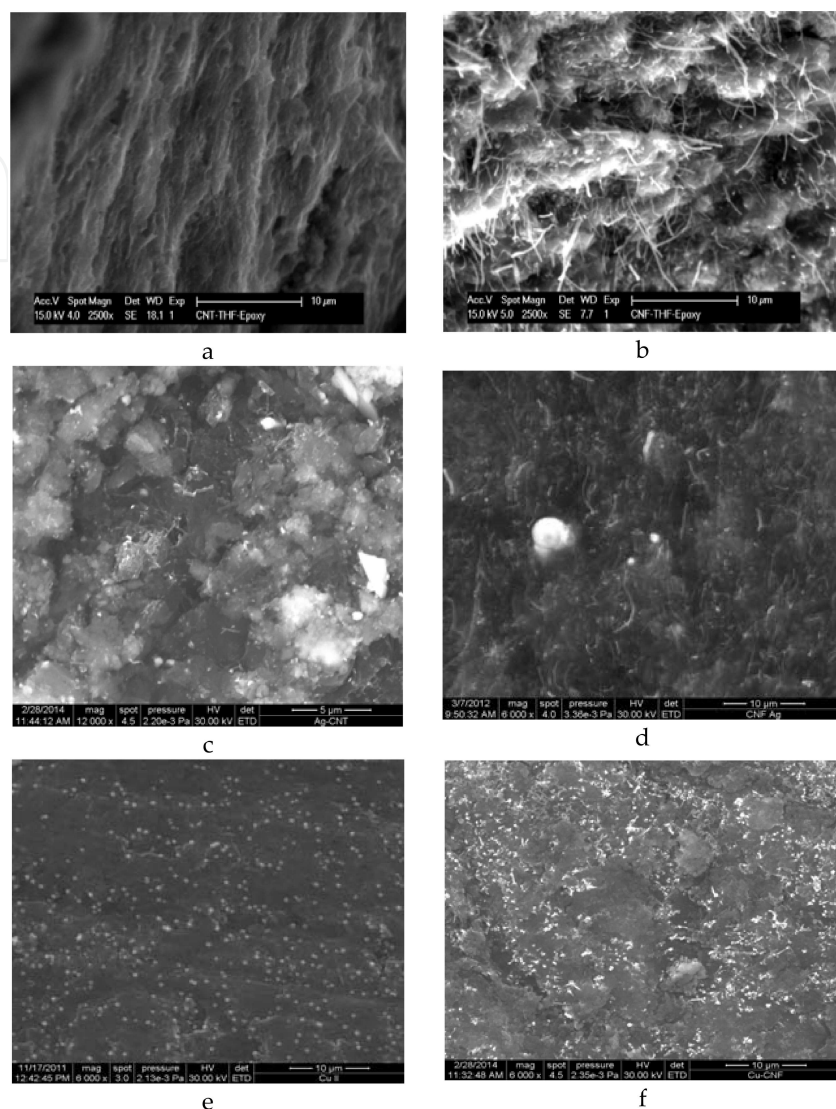


Figure 2. SEM image of NCC and M-NCC electrode surfaces: a)-CNT; b)-CNF; c)-AgCNT; d)-AgCNF; e)-CuCNT; f)-CuCNF.

2.1. Electrical and electrochemical properties of NCC electrodes

The electrical behavior of the NCC composite is an important property for the electrochemical detection application. For the composite electrode, the electrical property is given by the conductive filler loading within the insulating matrix and there is a percolation threshold loading beyond there is electrical conductivity. At low filler loading, the conductivity is very close to the pure insulating matrix conductivity because the fillers are dispersed individually or as small clusters in the matrix. Above the percolation threshold loading, independent conductive fillers tend to link together to form conductive networks, which leads to a significant increase of the electrical conductivity of the composite. Various percolation thresholds

for carbon nanotubes-based composites have been reported by various research groups, from 0.0025 %, wt. for carbon nanotubes-epoxy composites up to 5%, wt. [42]. Above this loading, the electrical conductivity increased very much until the carbon nanotubes reached 20%, wt. and beyond this loading no significant increasing of the electrical conductivity occurred.

In general, the electrical conductivity is measured by four-point probe resistance measurements (FPP), and some values for various NCC electrode surface are given in Table 2.

Electrode	Electrical conductivity (S cm^{-1})
CNT	0.596
CNF	0.247
AgCNT	0.602
AgCNF	0.320
CuCNT	0.605
CuCNF	0.319

Table 2. The electrical conductivity of several NCC and M-NCC electrode materials.

The presence of metallic nanoparticles enhanced slightly the electrical conductivity for the electrode materials. All electrode materials exhibit the electrical conductivity suitable for the electrochemical applications.

The electrochemical properties related to the electroactive surface area are studied by cyclic voltammetry (CV). CV is a very versatile electrochemical technique that allows to identify the aspects regarding the mechanism of redox system and transport properties of an electroactive species in solution. This technique is the first electrochemical experiment performed in order to characterize an electrode material for every type of application. This technique provides rapid information on the thermodynamic redox processes, on the kinetics of heterogeneous electron-transfer reactions, and on coupled chemical reactions or adsorption processes. This is accomplished with a three-electrode arrangement whereby the potential relative to some reference electrode is scanned at a working electrode, while the resulting current flowing through a counter (or auxiliary) electrode is monitored in a supporting electrolyte. The technique is ideally suited for a quick search of redox couples present in a system, and once located a couple may be characterized by more careful analysis of the cyclic voltammogram. Usually, the potential is scanned back and forward linearly with time between two extreme values using a triangular potential waveform.

The most common method to determine the electroactive surface area is the ferro/ferricyanide redox couple method [15]. Ferro/ferricyanide redox system gives rise to a reversible redox system that involves one electron per molecule. Given the one electron involving and chemical reversibility of the redox system, the cyclic voltammetric analysis of the ferro/ferricyanide process envisaged the determination of the electroactive area of the NCC and M-NCC

electrodes through the apparent diffusion coefficient of this redox system on these electrodes, calculated based on the Randles–Sevcik equation:

$$I_{pf} = (2.69 \times 10^5) n^{3/2} A D^{1/2} C^* v^{1/2} \quad (1)$$

Where n is the number of electrons involved in the redox process, A is the active area of the working electrode (cm^2), D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), C^* is the bulk concentration of the electroactive species (mol cm^{-3}), and v is the potential scan rate (V s^{-1}).

Thus, using cyclic voltammetry recorded at different scan rate in the presence of 4 mM $\text{K}_3\text{Fe}(\text{CN})_6$, the electrochemical behavior of ferrocyanide system is studied after CV recording (Figure 3), which offers the opportunity to determine the characteristics of a cyclic voltammetric response originating from a reversible process. The reversibility of the system was estimated by the peak-to-peak separation (the separation between the anodic peak potential and the cathodic peak potential, $\Delta E_p = E_{pa} - E_{pc}$). For a reversible couple the ΔE_p is equal to $0.059/n \text{ V}$ (n , the number of electron exchanged in the reaction, and in this case is equal with 1), and it is independent of the scan rate. For quasi-and irreversible conditions, the ΔE_p depends on the voltage scan rate. Another important parameter that is relates to the electrochemical reversibility of an electrode reaction is the peak current, and more specific, the ratio between the anodic peak current and the cathodic peak one (i_{pa}/i_{pc}), whose value is unity for a simple reversible couple.

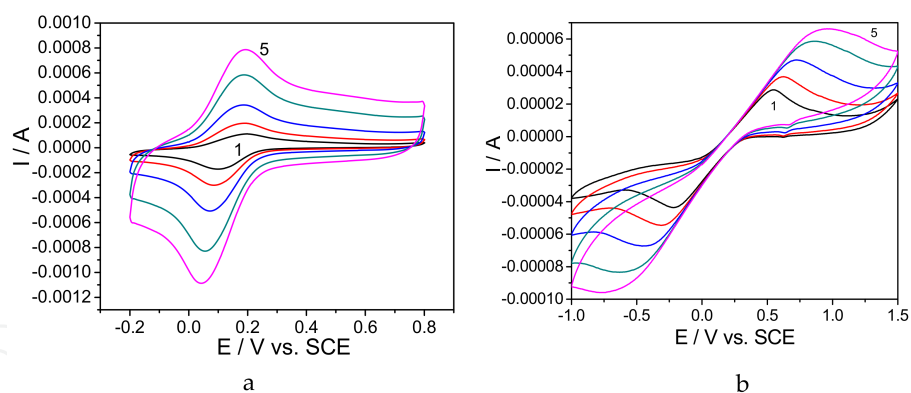


Figure 3. Cyclic voltammograms recorded at: a) CNT and b) Ag-CNT electrodes in the presence of 4 mM $\text{K}_3\text{Fe}(\text{CN})_6$ and 1M KNO_3 supporting electrolyte; potential scan rate: 1-0.025, 2-0.05, 3-0.1, 4-0.2, 5-0.3 Vs^{-1} ; potential range: -1 ÷ +1.5V/SCE.

By calculating diffusion coefficient based on the recorded voltammograms and comparing with theoretical diffusion coefficient ($6.7 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$), the values of the electroactive surface area can be determined. In general for all NCC and M-NCC the electroactive surface area are higher in comparison with the geometrical one. In addition, based on the reversibility parameters values, ΔE_p and i_{pa}/i_{pc} , some aspects regarding diffusion and adsorption process on the electrode surface can be elucidated, which must be correlated with the morphological, structural and electrical properties.

Also, other important aspects related to the electrochemical behaviour very important for electroanalysis are the potential window and the background currents. A large potential window and low background current are desired for the electrochemical detection applications. The background current is given by the capacitive component of the electrical double layer and it is desired that this component to be minimized. However, it is well-known that the electrode characterized by the electrocatalytic activity is characterized by high background current and low potential value for the oxygen evolution, which denotes a narrow potential window. Though, the electrodes characterized by the electrocatalytic activity are very useful for the detection application especial for the hard oxidizable or reduction species. In general, nanostructured carbon-based composite electrodes are characterized by low background current and large potential window (Figure 4a). However, it can be noticed that CNT exhibits higher background current and lower potential value for oxygen evolution, which can be attributed to a possible electrocatalytic effect towards this process. Metallic modified-carbon composite electrode exhibits the electrocatalytic activity towards oxygen evolution process, being characterized by higher background current and lower potential window (Figure 4b).

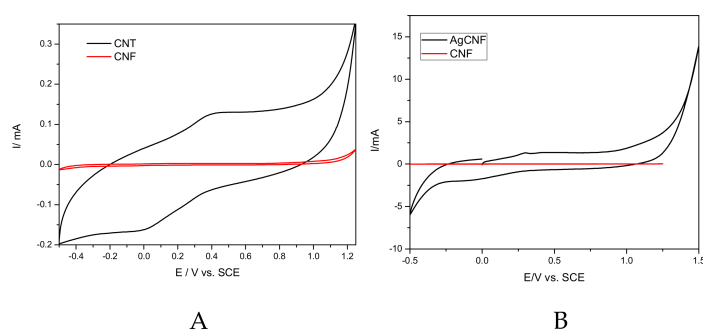


Figure 4. A. CVs recorded at a) CNF and b) CNT electrodes in 0.1 M Na_2SO_4 supporting electrolyte; scan rate 0.05Vs^{-1} . B. CVs recorded at a) CNF and b) AgCNF electrodes in 0.1 M Na_2SO_4 supporting electrolyte; scan rate 0.05Vs^{-1} .

3. Electrochemical techniques for the detection applications using NCC and M-NCC electrodes

3.1. Cyclic voltammetry

This technique is most useful technique to start the study of the detection applications for each type of the electrode material due to it provides information about the oxidation or reduction potential value, very important to optimize and simplify the detection procedure envisaging the batch injection analysis using chronoamperometry technique (BIA-CA), the easiest detection procedure. The information related to the electrochemical behaviours of NCC and M-NCC electrodes in the presence of various target analytes can be achieved by this technique, several examples will be given bellow. Also, some aspects about the mechanism elucidation related to the process control and adsorption aspects that are very useful for the detection application are provided by this technique operated at different scan rates.

3.1.1. Influence of scan rates

The oxidation or reduction processes of analytes on NCC and M-NCC electrodes are often very complex processes, involving both the adsorption of the reactant/intermediate or oxidation/reduction products and the formation of passive, nonconductive layer on their surface by electropolymerization or adsorption. The mechanistic aspects of the overall oxidation or reduction processes of target analyte on the electrode surface are elucidated using the cyclic voltammograms recorded at various scan rates ($0.01\text{--}0.2\text{ Vs}^{-1}$) in the presence of a certain concentration of the target analyte. As example, Figure 5a shows CVs recorded at CNF electrode in $0.1\text{ M Na}_2\text{SO}_4$ supporting electrolyte and the presence of 4 mM sulfide. The anodic current recorded at about $+0.7\text{ V}$ vs. SCE increased linearly with the square root of the scan rate (Figure 5b) suggesting that the reaction is mass-transfer controlled. No zero intercept inform about the adsorption process that can not be neglected. Moreover, the starting potential of the oxidation peak shifted towards positive potential when increasing v indicating that the electrooxidation process of sulfide is irreversible (Figure 5c) that is proved also, by the lack of the cathodic corresponding peak. In addition, CVs shapes informed about two steps of the sulfide oxidation process to elemental sulfur, both steps being diffusion-controlled.

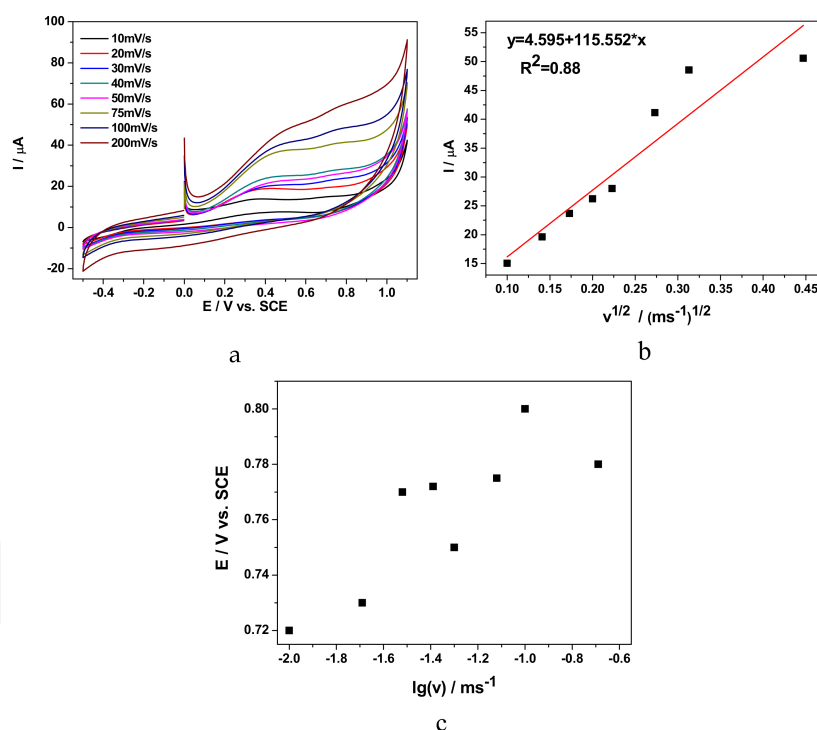


Figure 5. (a) CVs recorded at CNF electrode in $0.1\text{ M Na}_2\text{SO}_4$ supporting electrolyte and 0.5 mM sulfide with different scan rates: $0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.09, 0.1, 0.2\text{ Vs}^{-1}$ (curves 1-9); potential range: -0.5 and $+1.2\text{ V/SCE}$. (b) The anodic peak current recorded at $+0.7\text{ V/SCE}$ vs. square root of scan rate; (c) The peak potential E_p vs. $\lg(v)$.

Another example is given for the electrochemical behaviour of arsenic on AgCNF electrode (Figure 6) envisaging its detection. Arsenic (III) detection procedure involves anodic stripping voltammetry (ASV), which supposes two stages: first corresponding to reduction of arsenic

(III) at the electrode surface for a certain time followed by the second stage of electrochemically stripping from the electrode surface resulting a Faradaic response that is direct proportionally with arsenic concentration. The processes corresponding to these stages can be schematically represented by the following reactions [43]:

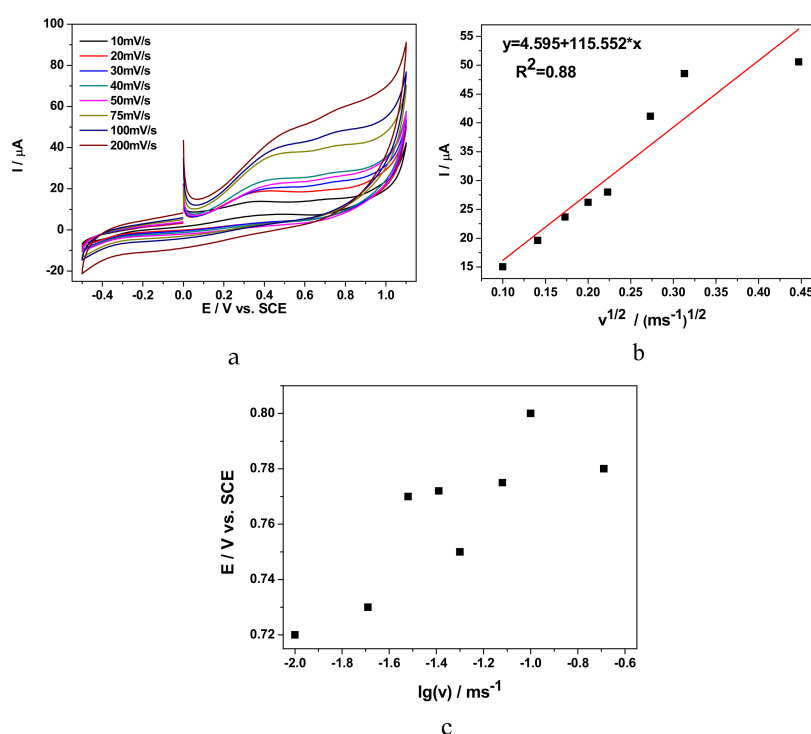
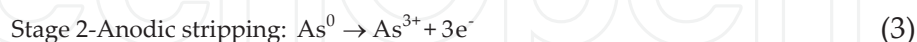


Figure 6. (a) CVs recorded at AgCNF electrode in 0.1 M Na_2SO_4 supporting electrolyte 0.09 M Na_2SO_4 +0.01 M H_2SO_4 supporting electrolyte and in the presence of 3 mM As with different scan rates: 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.09, 0.1, 0.2 Vs^{-1} (curves 1-9); potential range: -0.5 and $+1.2$ V/ SCE. (b) The anodic peak current recorded at $+0.7$ V/SCE vs. square root of scan rate; (c) The peak potential E_p vs. $\log(v)$.

The deposition stage for this procedure is achieved by maintaining the electrode potential at -0.4 V/SCE for 120 seconds. Based on the results regarding the CVs shapes, the linear dependence of anodic peak height versus the square root of the scan rate, the oxidation potential shifting to positive direction with increasing scan rate and the presence of the cathodic peak corresponding to the anodic one, arsenic stripping voltammetric process is quasi-reversible and diffusion-controlled. These results are promising for the application of these oxidation processes for the detection purposes.

3.1.2. CV for the detection application

CV technique is very useful for the detection applications. Figure 7 presents the results of the application of CNT electrode using CV for sulphide detection in various supporting electrolytes envisaging different practical applications. 0.1 M Na_2SO_4 supporting electrolyte has been chosen due to it is very common for the detection application in environmental application. 0.1 M Na_2SO_4 +1 M NaCl supporting electrolyte presents the composition very close to seawater and the question that raised was to check the possible interference of chloride anions. Real surface water was tested envisaging in-field detection application, for which no supporting electrolyte is added.

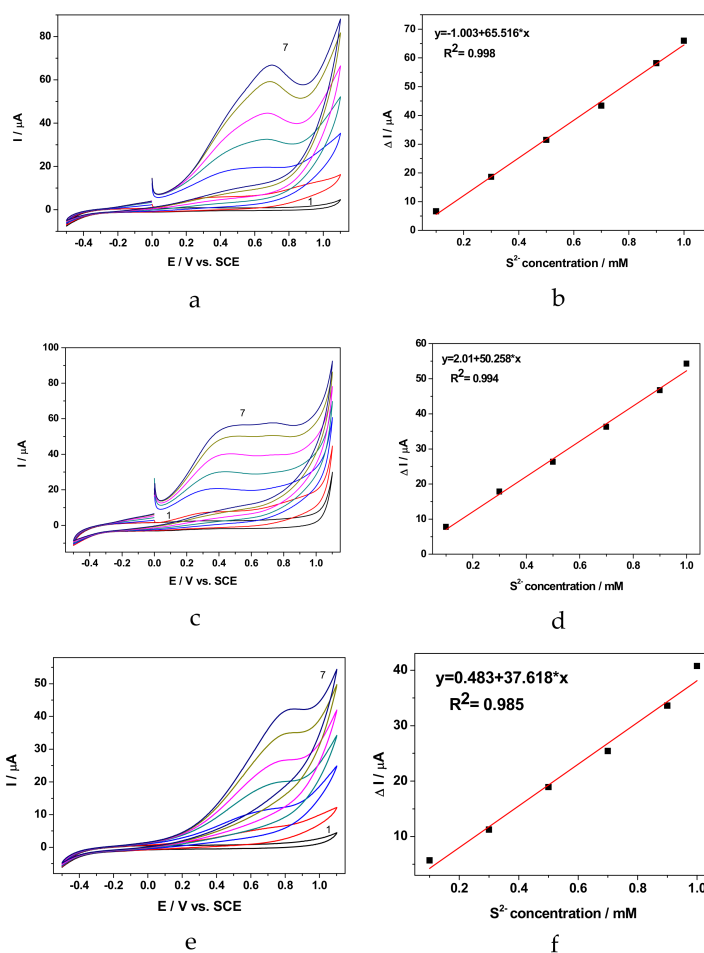


Figure 7. CVs recorded at CNT electrode in the presence of various sulfide concentrations 0.1; 0.3; 0.5; 0.7; 0.9; 1 mM in supporting electrolyte: 0.1 M Na_2SO_4 (a); 0.1 M Na_2SO_4 +1M NaCl (c); real surface water without adding supporting electrolyte. Calibration plots of the anodic current recorded at +0.7 V/SCE vs. sulfide concentrations for each supporting electrolytes (b, d, f).

CV results presented in Figure 7b informed that high concentration of chloride does not affect anodic current response characteristics to the sulfide detection, because the chlorine evolution occurred at high potential value. This result is very promising for sulfide detection in the seawater.

The literature data has been reported about the electrochemical behavior of carbon-based composite electrodes characteristics to ordered (array) or randomized micro/nanoelectrode ensembles characterized by the heterogeneous higher electroactivity [5, 44-49]. Sometimes, the voltammetric responses of carbon-based composite electrodes are sometimes similarly to that found for „edge effect”, which contribute significantly to the Faradaic current [5]. However, carbon-based composites obtained without a specific template are not rigorously arrays but are truly randomized ensembles, with the size, shape and inter-nano/micro carbon islands separation distributed over a wide range of insulating matrix. The random ensembles of microelectrodes can exhibit array behaviour in certain situation. Taking into consideration the distribution of the conductive filler islands within the insulator matrix, the main requirement is that the distance between individual conductive carbon microzones that should be much larger than its radius and mass transport is controlled by the spherical diffusion. The closely spaced carbon nano/microzones array will behave similar to a macroelectrode (linear diffusion-controlled mass transport) because of the diffusion layer overlap. Another important requirement is subjected to the insulating matrix to prevent current leakage, which resulted in the distortion of the cyclic voltammetry. Microelectrode arrays exhibit for the detection applications the advantages of single microelectrodes, e.g., reduced ohmic drop and charging current, the lower detection limit and better sensitivity. In the same time, their use overcomes the disadvantages of single microelectrode subjected to low current output and the high susceptibility to the electrochemical noise [47-49].

The above-presented CV results for the NCC and M-NCC obtained by two-roll mill procedure showed that these composite electrodes are not ordered (array) nano/microelectrodes, because it noticed the linear diffusion-controlled mass transport with a substantial hysteresis, explored by the scan rate influence of the CV shapes, which is characteristics to the macroelectrode behavior.

However, another practical micro/nanoelectrode array peculiarity is given by the ability to deliver the current responses in the absence of any supporting electrolyte, which is appropriate for in-situ or in-field detection applications. Even if the CV shapes recorded at NCC and M-NCC informed that these composites do not exhibit the array electrochemical behavior, however the similar anodic peak current for sulfide detection was noticed direct in surface water without supporting electrolyte at CNF composite electrode (Figure 7c). It can be seen that a slight lower sensitivity was found, and also, non considerable ohmic drop increasing was noticed in surface, which encourage the possible application for in-field sulfide detection.

3.2. Differential-pulsed voltammetry

Differential-pulsed voltammetry (DPV) is a very sensitive detection technique appropriate for trace levels of the analytes. The height of differential pulsed voltammogram is direct proportional to the concentration of analyte [27]:

$$i_p = \frac{nFAD^{1/2}C}{\sqrt{\pi t_m}} \left(\frac{1-\sigma}{1+\sigma} \right) \quad (4)$$

where $\sigma = \exp[(nF/RT)(\Delta E/2)]$, ΔE is the pulse amplitude.

The peak potential can identify the species especial for the simultaneous detection and the background current is much smaller in comparison with CV due to the charging current contribution is negligible. The optimization of the modulation amplitude (MA) and step potential (SP) operational parameters of DPV technique must be considered for each application in direct relation with the the sensitivity and the lowest limit of detection. Example of DPVs recorded on CNT in the presence of various pentachlorophenol (PCP) concentrations are shown comparatively with CV in Figure 8, and the electroanalytical parameters are gathered in Table 3. It can be noticed an improved detectability of PCP on CNT using DPV. Also, as we mentioned and expected, the detection peak potential is shifted to lower value, which is also very desired in electroanalysis.

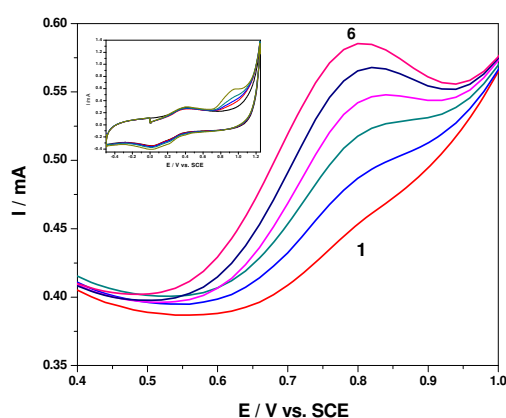


Figure 8. Differential-pulsed voltammograms recorded at CNT electrode (modulation amplitude 0.2 V, step potential 0.01 V) in 0.1 M Na_2SO_4 supporting electrolyte and in the presence of different pentachlorophenol concentration (20-120 μM) potential scan rate 0.05 Vs^{-1} and the potential range between 0 V and 1.25V vs. SCE

Peak potential	Technique used	Concentration range (μM)	Sensitivity ($\mu\text{A}/\mu\text{M}^{-1}$)	Correlation coefficient (R^2)	LOD (μM)
+ 0.97 V	CV	20-100	5.3	0.990	1.633
+ 0.80 V	DPV	20-120	11	0.984	0.801

Table 3. Electroanalytical performance of the CNT composite electrode for the detection of pentachlorophenol in 0.1M Na_2SO_4 supporting electrolyte.

The resolution for the simultaneous detection is improved by DPV measurements, sometimes being possible the detection of the analytes characterized by similar detection potential. An example of simultaneous detection of 4-chlorophenol (4-CP) and oxalic acid (OA) as its oxidation intermediar is given in Figure 9. The peak-shaped response coupled with the very low background current and the low detection potential values makes this technique involving NCC electrodes to be very useful for the simultaneous detection of the analytes.

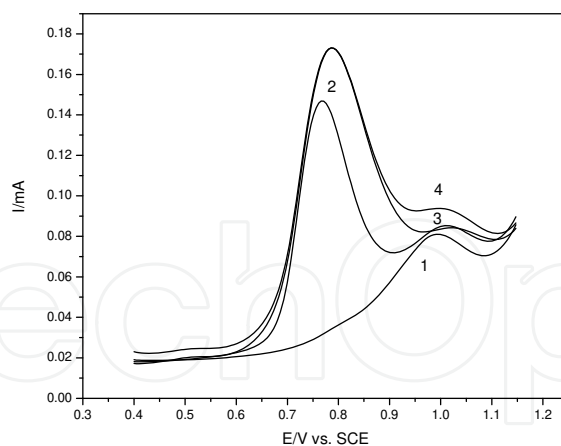


Figure 9. Simultaneous detection of 4-chlorophenol (4-CP) ($E=+0.8\text{V/SCE}$) and oxalic acid (OA) ($E=+1\text{ V/SCE}$) using CNF electrode: (1)-0.5 mM OA; (2)-0.5 mM OA+0.5 mM 4-CP; (3)-0.5 mM OA+0.6 mM 4-CP; (4)-0.6 mM OA+0.6 mM 4-CP.

3.3. Square-wave voltammetry

Square-wave voltammetry (SWV) is a large amplitude-differential technique characterized by a higher sensitivity than DPV, especial for the reversible system due to the reverse pulse cause the reverse reaction and the difference between the forward and reverse components are measured [27]. A very important advantage of this technique is the speed. The effective scan rate is given by $f\Delta E$, where f is frequency and ΔE is the step potential (SP). In comparison with DPV, for the detection of pentachlorophenol (PCP) the higher sensitivity was reached for 0.1 V MA, 0.01 V SP and 10 Hz frequency (see Table 4).

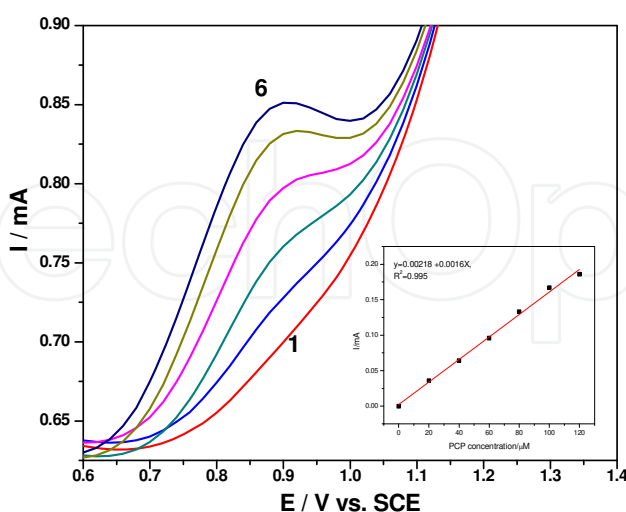


Figure 10. Square-wave voltammograms recorded at CNT electrode (modulation amplitude 0.1 V, step potential 0.01 V and frequency 10 Hz) in 0.1 M Na_2SO_4 supporting electrolyte and in the presence of different pentachlorophenol concentration (20-120 μM) potential scan rate 0.05 Vs^{-1} and the potential range between 0 V and 1.25V vs. SCE. Inset: Calibration plots of the anodic current recorded at $E=+0.95\text{ V/SCE}$ vs. PCP concentration.

The voltammetric techniques can be applied in a preconcentration/voltammetric detection scheme, which is useful for the detection of the trace levels of the analytes in direct relation with the electrode material. The adsorption property of the nanostructured carbon-based electrode towards the target analyte is not generally desired, because of electrode fouling and the loss of the electrode activity. However, this aspect could be exploited however in a positive way to detect organics at the trace level by applying the preconcentration/voltammetric detection scheme. The extent of preconcentration is a function of accumulation time, which determines the degree of adsorption on the electrode surface. The accumulation time represents the time of maintaining the potential value at an open-circuit potential (OCP) value [50]. As example, the effect of accumulation time on the currents of the square-wave anodic peaks recorded at +0.90 V/SCE corresponding to PCP oxidation was investigated. The enhancement factor of 10 determined as ratio of the peak current recorded after 30 minutes accumulation times to that recorded without a preconcentration scheme was found for 8 μ M PCP detection using CNT electrode. In Figure 11 is shown the SWVs recorded through the preconcentration-square-wave voltammetric technique. It can be noticed that preconcentration applying improved significantly the sensitivity (Table 4).

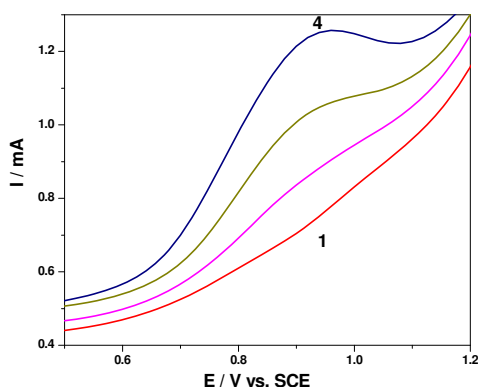


Figure 11. Square-wave voltammograms recorded at CNT electrode (modulation amplitude 0.1 V, step potential 0.01 V and frequency 10 Hz) in 0.1 M Na₂SO₄ supporting electrolyte and in the presence of different pentachlorophenol concentration (2-8 μ M) potential scan rate 0.05 Vs⁻¹ and the potential range between 0 V and 1.25V vs. SCE.

Peak potential	Technique used	Concentration range (μ M)	Sensitivity (μ A/ μ M ⁻¹)	Correlation coefficient (R ²)	LOD (μ M)
+ 0.80 V	DPV	20-120	11	0.984	0.801
+ 0.90 V	SWV	20-120	16	0.998	0.991
+ 0.95 V	Prec./SWV	2-8	138	0.952	0.033

Table 4. Electroanalytical performance of the CNT composite electrode using pulsed techniques for the detection of pentachlorophenol in 0.1M Na₂SO₄ supporting electrolyte.

3.4. Chronoamperometry

Chronoamperometry is the easiest electrochemical detection technique and it is appropriate for the practical detection applications. This technique is operated at the constant potential value, which is selected based on the existing well-established essential point of reference provided by the cyclic voltammograms, and the current-time dependence is monitored. As mass transport is controlled by diffusion, the current-time dependence reflects the change in the concentration gradient of the electrode surface vicinity. For macroelectrode characterized by linear diffusion, this technique should be used for diffusion coefficient determination and as consequence, for the specific electroactive surface area determination using Cottrell equation [27]:

$$i = \frac{nFACD^{1/2}}{\pi^{1/2}t^{1/2}} = kt^{-1/2} \quad (5)$$

For the detection application, the most common method is batch injection analysis (BIA), where the amperometric response recorded by chronoamperometry is obtained for successive and continuous addition of a certain concentration of the analyte. Figure 12 shows the amperometric response (BIA) recorded at AgCNF electrode in 0.1 M Na₂SO₄ supporting electrolyte by adding 2.4 μM ibuprofen (IBP) at an applied potential of 1.1 V vs. SCE. The response of the electrode is linear in the concentration range of 2.4 μM to 21.6 μM IBP (Inset of Fig. 12).

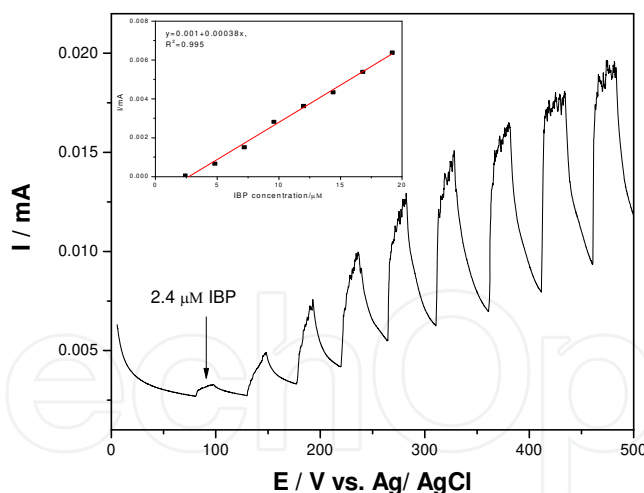


Figure 12. Amperometric response-batch system analysis (BIA) of the Ag-CNF electrode for the successive and continuous addition of 2.4 μM IBP. Applied potential: 1.1 V vs. SCE. Inset: calibration plots of useful signal vs. IBP.

3.5. Pulsed-amperometry

Pulsed-amperometry is an alternative for chronoamperometry to overcome the disadvantage of the electrode fouling during the detection application. In different working programs applied in practice of the pulsed amperometric detection (PAD) the measurement potential is

kept for a short time (measurement pulse) after the electrode cleaning pulse and conditioning potential pulse [51]. This technique has proved to be extremely sensitive for the detection of organic molecules because of the advantage of *in-situ* cleaning and reactivating the electrode surface during the electroanalytical detection [52].

PA technique is very useful for the practical detection application especial for the detection of the analytes that can be very easily adsorbed on the electrode surface causing electrode fouling. Application of this technique for the detection of pentachlorophenol at CNT electrode as alternative for CA allowed achieving one hundred times better sensitivity under the operating conditions of three potential pulses, whose values were established on CV behaviour. The pulses were applied continuously using the following scheme [24]:

- *Pulse 1* operated at +0.97 V/SCE for a duration of 50 ms, where PCP is directly oxidized on the electrode surface,
- *Pulse 2* operated at +1.25 V/SCE for a duration of 50 ms, considered as cleaning potential because O_2 evolution occurred,
- *Pulse 3* operated at -0.1 V/SCE for a duration of 50 ms, where the electrode surface involved-reduction process occurred.

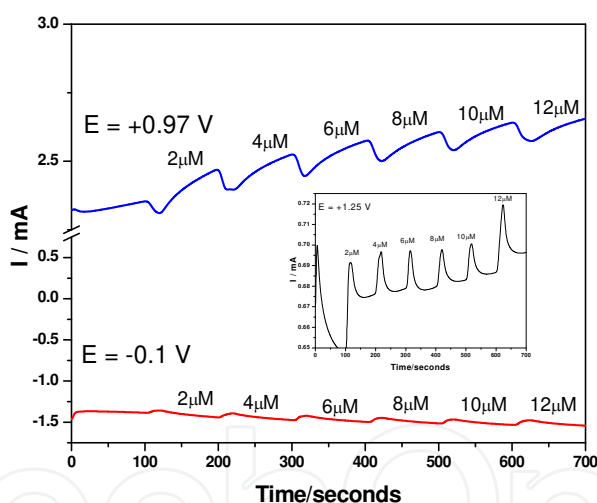


Figure 13. Pulsed amperograms (PAs) recorded at CNT electrode in 0.1 M Na_2SO_4 supporting electrolyte for the successive and continuous addition of 2 μM PCP recorded at $E=+1.25$ V; +0.97 and -0.1 V vs. SCE.

4. Conclusions

Electrochemical techniques should be regarded as suitable tools for the electrochemical characterization and the detection applications of the nanostructured carbon composite (NCC) and metallic nanoparticles-modified nanostructured carbon composite (M-NCC) electrodes. Cyclic voltammetry (CV) is very useful for the electrochemical characterization that provided

mechanistic information based on which the operating conditions are optimized. In general, CV results are considered as reference for the all electrochemical technique applied in the detection application, especially for chronoamperometry (CA) and pulsed amperometry (PA). NCC and M-NCC electrodes obtained by two-roll mill procedure are very promising materials for the detection applications, due to fascinating properties of the nanostructured carbon and metallic nanoparticles. The electrode morphology affected the electrical and electrochemical behaviour of the electrode materials. Their electrochemical detection performances are linked to the electrochemical technique specificity, the best results being achieved using pulsed voltammetric techniques (DPV and SWV). These techniques are very effective also, for the simultaneous detection of multi-components. However, for the practical detection application, CA is most useful due to its simplicity but sometimes, for the specific process that occurred on the electrode surface during the detection, this technique favours the electrode fouling and as consequence, the loss of the electrode activity. PA overcomes the electrode fouling disadvantage since in-situ electrochemical cleaning can be assured by applying simultaneously the potential at which desired advanced oxidation/reduction as cleaning step and mild oxidation/reduction for electrode stabilizing besides the detection potential.

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